

DESCRIPTIONNANOSCALE FACETED POLYHEDRA

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Cross-Reference to Related Applications

This application claims the benefit of provisional patent application Serial No. 60/270,998, filed February 23, 2001, and provisional patent application Serial No. 60/314,855, filed August 24, 2001.

Background of the Invention

[0001] Design principles that are based upon the concepts of crystal engineering and self-assembly have recently afforded new classes of crystalline solids that possess important physical properties such as bulk magnetism or porosity. Large-scale molecular networks have been developed to encapsulate other materials and these are playing an ever-increasing role in the pharmaceutical industry and as materials for sensors, and liquid crystals. In addition, with the inclusion of metals within the structures, the large polymers formed by these crystals have magnetic properties as well as exhibiting catalytic properties.

[0002] In recent years, chemists have developed synthetic design strategies that are based on the concept of self-assembly. This supramolecular approach to synthesis has afforded a new generation of discrete, high molecular weight compounds. These compounds are exemplified by nanoscale spheroid architectures that are based upon Platonic, or regular, and Archimedean, or semi-regular, solids. Nanoscale versions of Platonic and Archimedean solids have been prepared wherein their building blocks, molecular polygons, are connected at their edges. Closed convex polyhedra are generated in this manner.

[0003] In contrast to the Platonic and Archimedean solids that have been generated by edge-sharing of molecular polygons, it would be advantageous to produce open-shell polyhedra,

which would necessarily be porous in a predictable manner, and thus be susceptible to a high degree of control over structure and functionality.

Brief Summary of the Invention

[0004] The subject invention pertains to molecular polyhedra constructed of molecular building blocks that approximate polygons (hereinafter molecular polygons), in which the molecular polygons are linked at their vertices. The molecular polygons can comprise metal-organic moieties (also termed nanoscale secondary building units, or nSBUs) or non-metal-organic moieties. The molecular polyhedra of the subject invention provide several advantages over nanoscale solids that are based on conventional Platonic (regular) and Archimedean structures, which are constructed of building blocks linked at their edges.

[0005] The molecular polyhedra and polymeric structures of the subject invention can be constructed of molecular polygons (such as triangles, squares, and other polygons), wherein the molecular polygons are linked at their vertices by a linking molecular moiety that subtends the appropriate angle between the planes of the linked molecular polygons. By virtue of the vertex-linkages between their component polygons, the molecular polyhedra of the subject invention can have open faces (faceted polyhedra), and can therefore exhibit desirable physical properties, such as porosity. nSBU vertices can be linked via covalent interactions using the coordinating ligands exemplified herein, such as bifunctional or trifunctional carboxylates, as well as other appropriate coordinating ligands. Appropriate coordinating ligands include those angular multifunctional ligands capable of sustaining the desired dihedral angle(s) between nSBUs. Molecular polygons comprising non-metal-organic moieties can be linked at their vertices via non-covalent interactions through bridging ligands. Appropriate bridging ligands include those angular ligands capable of sustaining the desired dehedral angle(s) between non-metal polygons. nSBUs vertices can be linked to vertices of non-metal polygons through bridging ligands, using non-covalent interactions. The appropriate bridging ligands include those angular ligands capable of sustaining the desired dihedral angle(s) between the metal polygon and the non-metal polygon. Preferably, the bridging ligand is a multifunctional molecular moiety capable of sustaining multiple supramolecular interaction.

[0006] The subject invention further pertains to compounds comprising the molecular polyhedra described herein. The molecular polyhedra can be utilized to generate a wide variety of compositions in an efficient and predictable manner.

[0007] The molecular polygons used to construct the polyhedra of the subject invention are preferably, but not limited to, metal-organic moieties (nSBUs). Advantages inherent in the utilization of nSBUs include: (i) metal-organic coordination polymers can be prepared via self-assembly, allowing inexpensive synthesis, often with one step and high yield (*e.g.*, “one pot” reactions); structures having metal-organic building blocks are inherently modular since they contain at least two components, a node (such as an nSBU) and a “spacer” (such as a multifunctional organic coordinating ligand); structures having metal-organic building blocks can have an open framework, which conveys the ability to gain very precise control over cavities and channels; metal organic coordination polymers are typically of low solubility and, therefore, kinetic and thermodynamic products can be formed for a particular set of components, making them useful for sorption from, and to, solution phases; and metal-organic incorporating structures tend to be moderately thermally stable and air and water stable (many compounds of the subject invention are stable to 200°C and others are stable at or above 400°C). In addition, the use of metal-organic building blocks are particularly useful for the construction of molecular polyhedra (and compounds comprising such molecular polyhedra) that can exhibit one or more advantageous properties, such as magnetic activity, luminescent activity, phosphorescent activity, fluorescent activity, and catalytic and redox activity.

[0008] The subject invention also concerns methods of producing polyhedron-shaped molecules with polygons, such as metal-organic polygons, or non-metal-organic polygons, linked at their vertices. The methods of the subject invention can involve as little as one self-assembly reaction, where inexpensive, commercially available reagents can be utilized.

[0009] Examples of general formulas for polyhedron molecules and polymeric structures of the subject invention that are constructed from metal-organic polygons (nSBUs) include:

[0010] Formula 1: (MA)₁₂

[0011] Formula 1 represents a general formula for molecules of the subject invention having a spheroid architecture (*e.g.*, nanoballs) (90°) of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, A is a bifunctional carboxylate that

subtends an angle of 90° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0012] Examples of bifunctional carboxylates that can subtend an angle of 90° are shown in Figures 24A-24C. The angle subtended by the bifunctional carboxylate in Figure 24B is actually 72°, but can sustain distortion to 90°, as determined by molecular modeling experiments.

[0013] Formula 2: $(MA)_{24}$

[0014] Formula 2 represents a general formula for nanoballs (120°) of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, wherein A is a bifunctional carboxylate that subtends an angle of 120° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0015] Formula 3: $(MA)_{60}$

[0016] Formula 3 represents a general formula for nanoballs (144°) of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, wherein A is a bifunctional carboxylate that subtends an angle of 144° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0017] Formula 4: $(MA)_n$

[0018] Formula 4 represents a general formula for a square (tetragonal) 2D network or lattice of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, A is a bifunctional carboxylate that subtends an angle greater than 90°, and preferably subtends an angle of 120°, allowing for geometric distortion, wherein 'n' indicates a polymeric structure, albeit in two dimensions (*i.e.*, $n \geq 4$), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0019] Formula 5: $(MA)_n$

[0020] Formula 5 represents a general formula for hexagonal (Kagomé) 2D network or lattice of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, wherein A is a bifunctional carboxylate that subtends an angle greater than 90°, and preferably subtends an angle of 120°, allowing for geometric distortion, wherein 'n' indicates a polymeric structure, albeit in two dimensions (*i.e.*, $n \geq 3$), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0021] Formula 6: $(M^1_4M^2_3A_3Y_2)_n$

[0022] Formula 6 represents a general formula for an embodiment of a polymer of the subject invention, as shown in Figures 11A-11F, wherein M^1 can be any metal that can sustain 3-fold rotational symmetry, wherein M^2 can be any metal that can sustain 4-fold rotational symmetry, wherein A is a trifunctional carboxylate with 3-fold rotational symmetry (allowing for geometric distortion), wherein Y is any -1 anion ("Y₂" could also be just one "Y", if Y is a -2 anion), wherein 'n' indicates a polymeric structure in three dimensions (*i.e.*, n ≥ 2), and wherein any coordinating ligand or solvent molecule is optionally coordinated to each M.

[0023] Formula 7: $(M_3A_2)_n$

[0024] Formula 7 represents a general formula for another embodiment of a polymer of the subject invention, as shown in Figures 15A-15F, wherein M can be any metal that can sustain 4-fold rotational symmetry, wherein A is a trifunctional carboxylate with 3-fold rotational symmetry (allowing for geometric distortion), wherein 'n' indicates a polymeric structure in three dimensions (*i.e.*, n ≥ 2), and wherein any coordinating ligand or solvent molecule is optionally coordinated to each M.

[0025] In each of the above Formulas 1-7, M is a metal preferably in its 2+ transition state. However, it is also contemplated that M can be in other transition states (such as 1+, 3+, and so forth), and structures of the subject invention can contain M in more than one transition state (*i.e.*, M(II)M(III)). For every M that is not in a 2+ transition state, there will preferably exist a counter ion to balance the charge (+ charge if < 2; - charge if > 2). The anions may, or may not, be coordinated to the metal.

Brief Description of Drawings

[0026] **Figures 1A-1C** show cubohemioctahedron, small rhombihexahedron and small rhombidodecahedron uniform polyhedra, respectively, formed by linking vertices of squares only.

[0027] **Figures 2A-2NN** illustrate representative ligands for 120°.

[0028] **Figures 3A-3G** illustrate representative ligands for 144°.

[0029] **Figure 4** shows the square nanoscale secondary building unit (nSBU), described by the general formula, M₂(RCO₂)₄, such as [Cu₂(PhCOO)₄]. Figure 4 (left) shows a ball-and-

stick model of a square nSBU. Figure 4 (right) shows the corresponding conformational projection for this molecule.

[0030] **Figures 5A-5G** show various orientations of an Archimedean faceted nanoball configuration. Figures 5A-5D illustrate the linking of molecular squares and Figures 5E-5G show space-filling models of the Archimedean faceted nanoball.

[0031] **Figures 6A-6J** show various orientations of an isomer configuration of the Archimedean faceted nanoball shown in Figures 5A-5G. Figures 6A-6G illustrate the linking of molecular squares and Figures 6H-6J show space-filling models of the isomer configuration.

[0032] **Figures 7A-7C** show space-filling and schematic representations of the arrangement of square nSBUs in the nanoscale square lattice structure described in Example 16.

[0033] **Figures 8A-8C** show space-filling and schematic representations of the arrangement of triangular nSBUs in the nanoscale Kagomé lattice structure described in Example 15.

[0034] **Figure 9** shows a further embodiment of the invention, a triangular (nSBU). Figure 9 (left) shows a ball-and-stick model of a triangular nSBU. Figure 9 (right) shows the corresponding conformational projection for this molecule.

[0035] **Figures 10A-10I** show a schematic with illustrations of nine faceted polyhedra of the instant invention. Figure 10A shows a molecular polyhedron of the subject invention with triangular polygons linked at their vertices with a dihedral angle of 70° and 32' (wherein ' equals minutes). Figure 10B shows a molecular polyhedron with square polygons linked at their vertices with a dihedral angle of 90° dihedral angle. Figure 10C shows a molecular polyhedron with triangular polygons linked at their vertices with a dihedral angle of 109° and 28'. Figure 10D shows a molecular polyhedron with square polygons linked to triangular polygons with a dihedral angle of 125° and 16'. Figure 10E shows a molecular polyhedron with square polygons linked at their vertices with a dihedral angle of 120°. Figure 10F shows a molecular polyhedron with triangular polygons linked at their vertices with a dihedral angle of 138° and 11'. Figure 10G shows a molecular polyhedron with molecular pentagons linked at their vertices with a dihedral angle of 160° and 34'. Figure 10H shows a molecular polyhedron with molecular polyhedrons linked to molecular triangles with a dihedral angle of 142° and 37'. Figure 10I shows a molecular polyhedron with molecular squares linked at their vertices with a dihedral angle of 144°.

[0036] **Figures 11A-11C and 11D-11F** show two further examples, respectively, of networks derived from the crystal structures of the instant invention.

[0037] **Figures 12A-12C** show schematic illustrations of three uniform space filling models based on Platonic and Archimedean polyhedra that are possible for faceted polyhedra.

[0038] **Figures 13A and 13B** show a schematic illustration of how the small cubicuboctahedron and the small rhombihexahedron have a congruent edge-skeleton with the Archimedean polyhedron, the rhombicuboctahedron. In Figure 13A, a rhombicuboctahedron (left) and its edge-skeleton (right) are shown. In Figure 13B, a small cubicuboctahedron (left) and a small rhombihexahedron (right) are shown.

[0039] **Figures 14A and 14B** show an illustration of how the vertices of the molecular squares and triangles are connected by the benzene tri-carboxylic moieties. Molecular squares and triangles are shown in Figure 14A. Only molecular squares are shown in Figure 14B.

[0040] **Figures 15A-15F** show another polyhedra formed containing zinc as the metal in the structure.

[0041] **Figure 16** shows the chemical bonds of a sphere according to the subject invention.

[0042] **Figure 17** shows a distorted version of the molecule of Figures 6A-6J.

[0043] **Figures 18A and 18B** are a schematic representation of triangular and Kagomé lattices, respectively.

[0044] **Figures 19A and 19B** are other representations of square and triangular nSBUs, respectively, that can be formed by linking the vertices of molecular squares.

[0045] **Figures 20A and 20B** show the magnetic properties of the structure described in Example 15. Figure 20A shows the temperature-dependent molar susceptibility (per nSBU), χ , of the structure of Example 15 at a 0.1 Tesla (data points) overlaid by a plot of the Bleaney-Bowers best fit model (solid line): $J = -350 \text{ cm}^{-1}$ and $J' = -18 \text{ cm}^{-1}$. Figure 20B shows the field-dependent magnetization of the structure of Example 15 at $T = 5 \text{ k}$.

[0046] **Figures 21A and 21B** show the magnetic properties of Example 16. Figure 21A shows the temperature-dependent molar susceptibility (per nSBU), χ , of the structure of Example 16 at a 0.1 Tesla (data points) overlaid by a plot of the Bleaney-Bowers best fit model (solid line): $J = -380 \text{ cm}^{-1}$ and $J' = -85 \text{ cm}^{-1}$. Figure 21B shows the field-dependent magnetization of the structure of Example 16 at $T = 5 \text{ k}$.

[0047] **Figure 22** shows an example of the conformation of a benzene-1,3-dicarboxylate (bdc) ligand that produces the 0D (discrete) nanoballs of the subject invention.

[0048] **Figure 23** shows an example of the conformation of a bdc ligand that produces 2D networks (square and Kagomé) of the subject invention.

[0049] **Figures 24A-24C** show examples of bifunctional carboxylates that subtend an angle of 90°. The angle subtended by the bifunctional carboxylate in Figure 24B is actually 72°, but can sustain distortion to 90°, as determined by molecular modeling experiments.

[0050] **Figure 25** shows an AFM image of microcrystals on glass after annealing at 37°C for 24 hours.

[0051] **Figure 26** shows an AFM image of microcrystals on glass after annealing at 75° for 24 hours.

[0052] **Figure 27** shows an example of a molecular polygon that does not comprise a metal-organic moiety. The molecular polygon shown is a non-metal molecular square.

[0053] **Figure 28** shows another example of a molecular polygon that does not comprise a metal-organic moiety. The molecular polygon shown is a non-metal molecular triangle.

[0054] **Figure 29** shows an example of a bridging ligand (1,3-dihydroxybenzene) that subtends an angle of about 120°. The bridging ligand shown can be utilized, for example, to link the non-metal molecular polygons shown in Figures 27 and 28.

Detailed Disclosure of the Invention

[0055] The subject invention pertains to molecular polyhedra constructed of molecular building blocks that approximate polygons (hereinafter molecular polygons), in which the molecular polygons are linked at their vertices. The molecular polygons can comprise metal-organic moieties (also termed nanoscale secondary building units, or nSBUs) or non-metal-organic moieties. The molecular polyhedra of the subject invention can be constructed of molecular polygons (such as triangles, squares, and other polygons), wherein the molecular polygons are linked at their vertices by a linking molecular moiety that subtends the appropriate angle between the planes of the linked molecular polygons.

[0056] By virtue of the vertex-linkages between their component polygons, the molecular polyhedra and polymeric structures of the subject invention can have open faces (faceted polyhedra), and can therefore exhibit desirable physical properties, such as porosity. nSBU

vertices can be linked via covalent interactions using the coordinating ligands exemplified herein, such as bifunctional or trifunctional carboxylates, as well as other appropriate coordinating ligands. Appropriate coordinating ligands include those angular multifunctional ligands capable of sustaining the desired dihedral angle(s) between nSBUs. Molecular polygons comprising non-metal-organic moieties can be linked at their vertices via non-covalent interactions through bridging ligands. Appropriate bridging ligands include those angular ligands capable of sustaining the desired dehedral angle(s) between non-metal polygons. nSBUs vertices can be linked to vertices of non-metal polygons through bridging ligands, using non-covalent interactions. The appropriate bridging ligands include those angular ligands capable of sustaining the desired dihedral angle(s) between the metal polygon and the non-metal polygon.

[0057] The nanoscale polyhedra of the subject invention can exist as discrete macromolecules or be fused, *e.g.*, in order to crystal engineer open framework solids.

[0058] Examples of general formulas for polyhedron molecules and polymeric structures of the subject invention that are constructed of metal-organic polygons (nSBUs) include:

[0059] Formula 1: $(MA)_{12}$

[0060] Formula 1 represents a general formula for molecules of the subject invention having a spheroid architecture (*e.g.*, nanoballs) (90°), wherein M can be any metal that can sustain 4-fold rotational symmetry (such as a molecular square), A is a bifunctional carboxylate that subtends an angle of 90° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0061] Examples of bifunctional carboxylates that can subtend an angle of 90° are shown in Figures 24A-24C. The angle subtended by the bifunctional carboxylate in Figure 24B is actually 72° , but can sustain distortion to 90° , as determined by molecular modeling experiments.

[0062] Formula 2: $(MA)_{24}$

[0063] Formula 2 represents a general formula for nanoballs (120°) of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry (such as a molecular square), wherein A is a bifunctional carboxylate that subtends an angle of 120° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0064] Formula 3: $(MA)_{60}$

[0065] Formula 3 represents a general formula for nanoballs (144°) of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, wherein A is a bifunctional carboxylate that subtends an angle of 144° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0066] Formula 4: $(MA)_n$

[0067] Formula 4 represents a general formula for a tetragonal 2D network of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry (such as a molecular square), A is a bifunctional carboxylate that subtends an angle greater than 90°, and preferably subtends an angle of 120°, allowing for geometric distortion, wherein 'n' indicates a polymeric structure, albeit in two dimensions (*i.e.*, $n \geq 4$), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0068] Formula 5: $(MA)_n$

[0069] Formula 5 represents a general formula for Kagomé 2D network of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, wherein A is a bifunctional carboxylate that subtends an angle greater than 90°, and preferably subtends an angle of 120°, allowing for geometric distortion, wherein 'n' indicates a polymeric structure, albeit in two dimensions (*i.e.*, $n \geq 3$), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0070] Formula 6: $(M^1_4M^2_3A_3Y_2)_n$

[0071] Formula 6 represents a general formula for an embodiment of a polymer of the subject invention, as shown in Figures 11A-11F, wherein M^1 can be any metal that can sustain 3-fold rotational symmetry (such as a molecular triangle), wherein M^2 can be any metal that can sustain 4-fold rotational symmetry, wherein A is a trifunctional carboxylate with 3-fold rotational symmetry (allowing for geometric distortion), wherein Y is any -1 anion ("Y₂" could also be just one "Y", if Y is a -2 anion), wherein 'n' indicates a polymeric structure in three dimensions (*i.e.*, $n \geq 2$), and wherein any coordinating ligand or solvent molecule is optionally coordinated to each M.

[0072] Formula 7: $(M_3A_2)_n$

[0073] Formula 7 represents a general formula for another embodiment of a polymer of the subject invention, as shown in Figures 15A-15F, wherein M can be any metal that can sustain

4-fold rotational symmetry (such as a molecular square), wherein A is a trifunctional carboxylate with 3-fold rotational symmetry (allowing for geometric distortion), wherein 'n' indicates a polymeric structure in three dimensions (*i.e.*, $n \geq 2$), and wherein any coordinating ligand or solvent molecule is optionally coordinated to each M.

[0074] In each of the above Formulas 2-7, M can be any transition metal and is preferably in its 2+ transition state. It is also contemplated that M can be in other transition states (such as 1+, 3+, and so forth), and structures of the subject invention can contain M in more than one transition state (*i.e.*, M(II)M(III)). For every M that is not in a 2+ transition state, there will preferably exist a counter ion to balance the charge (+ charge if < 2 ; - charge if > 2). The anions may, or may not, be coordinated to the metal.

[0075] Examples of metals that can sustain 3-fold rotational symmetry include, but are not limited to, metals that sustain tetrahedral, trigonal pyramidal, trigonal bipyramidal, or trigonal planar coordination spheres. Examples of first row transition metals (from the periodic table of the elements) that meet this criterion include Zn(II), Cr(IV), Cr(V), Cr(VI), Co(II), Tc(VII), Mn(II), Fe(II), Fe(V), Ni(II), and Cu(II). Preferred metals that can sustain 3-fold rotational symmetry include, for example, Zn(II), Co(II), Ni(II), Fe(II), Cu(II), and Mn(II). Examples of metals that can sustain 4-fold rotational symmetry include, but are not limited to, ions that sustain octahedral, square planar, or square pyramidal coordination spheres. Examples of first row transition metals (from the periodic table of the elements) that meet this criterion include Ti(III), V(III), Cr(II), Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). Preferred metals that can sustain 4-fold rotational symmetry include, for example, Cr(II), Co(II), Fe(II), Ni(II), Cu(II), and Zn(II).

[0076] Bifunctional carboxylates that can subtend an angle of 90° include, but are not limited to, those shown in Figures 24A-24C.

[0077] Bifunctional carboxylates that can subtend an angle of 120° include, but are not limited to, those shown in Figures 2A-2NN. Preferred bifunctional carboxylates that can subtend an angle of 120° include 1,3-benzenedicarboxylate, 5-hydroxy-1,3-benzenedicarboxylate, 5-nitro-1,3-benzenedicarboxylate, and 5-alkyl-1,3-benzenedicarboxylates.

[0078] Bifunctional carboxylates that can subtend an angle of 144° include, but are not limited to, those shown in Figures 3A-3G. Preferred bifunctional carboxylates that can subtend

an angle of 144° include 2,4-pyrroledicarboxylate, *N*-methyl-2,4-pyrroledicarboxylate, 2,4-furandicarboxylate and 1,3-cyclopentadien dicarboxylate.

[0079] Trifunctional carboxylates that can sustain 3-fold rotational symmetry include, but are not limited to 2-, 4- and/or 6-substituted 1,3,5-benzenetricarboxylates. Preferred trifunctional carboxylates that can sustain 3-fold rotational symmetry include 1,3,5-benzenetricarboxylate.

[0080] Additional examples of general formulas for polyhedron molecules of the subject invention that are constructed of metal-organic polygons (nSBUs) include: Formula 8: $(M_4A_3)_2$, which is a tetrahemihexahedron, shown in Figure 10A; Formula 9: $(M_4A_3)_4$, which is a octahemioctahedron, shown in Figure 10C; Formula 10: $(M_7A_6)_4$, which is a small cubicuboctahedron, shown in Figure 10D; Formula 11: $(M_4A_3)_{10}$, which is a small icosihemidodecahedron, shown in Figure 10F; and Formula 12: $(M_{16}A_{15})_4$, which is a small dodecicosidodecahedron, shown in Figure 10H.

[0081] Examples of general formulas for polyhedron molecules of the subject invention that are constructed of non-metal-organic polygons include: Formula 13 (a small rhombidodecahedron): $S_{12}B_{24}$, wherein S is a non-metal molecular square, such as that shown in Figure 27, and B is a bridging ligand, such as that shown in Figure 29; and Formula 14 (small cubicuboctahedron): $S_6T_8B_{24}$, wherein S is a non-metal molecular square, such as that shown in Figure 27, T is a non-metal molecular triangle, such as that shown in Figure 28, and B is a bridging ligand, such as that shown in Figure 28.

[0082] The molecular building blocks of the present invention are preferably, but not limited to, those containing metal-organic moieties (nSBUs). Advantages inherent in the utilization of nSBUs include: (i) metal-organic coordination polymers can be prepared via self-assembly, allowing inexpensive synthesis, often with one step and high yield (e.g., “one pot” reactions); structures having metal-organic nSBUs are inherently modular since they contain at least two components, a node (e.g., the nSBU) and a “spacer” (e.g., a multifunctional organic coordinating ligand); structures having nSBUs can have an open framework, which conveys the ability to gain very precise control over cavities and channels; metal organic coordination polymers are typically of low solubility and, therefore, kinetic and thermodynamic products can be formed for a particular set of components, making them useful for sorption from, and to, solution phases; and metal-organic incorporating structures tend to be moderately thermally stable and air and water stable (many compounds of the subject invention are stable to 200°C and

others are stable at or above 400°C). In addition, the use of nSBUs are particularly useful for the construction of molecular polyhedra (and compounds comprising such molecular polyhedra) that can exhibit one or more advantageous properties, such as magnetic activity, luminescent activity, phosphorescent activity, fluorescent activity, and catalytic and redox activity.

[0083] The subject invention also concerns molecular polyhedron molecules that are constructed of building blocks that are not based upon metal-organic moieties. Polyhedron-shaped molecules of the subject invention can be constructed from any molecular, or supramolecular, moieties that approximate molecular polygons, and which can be connected by a linking molecular moiety that subtends the appropriate angle. Examples of molecular building blocks that do not comprise metal-organic moieties are shown in Figure 27 (non-metal molecular square) and Figure 28 (non-metal molecular triangle). Figure 29 shows an example of a bridging ligand that is appropriate to connect the vertices of non-metal molecular polygons, such as those shown in Figures 27 and 28, and which subtends an angle of about 120°.

[0084] Edge-sharing of molecular polygons affords closed convex polyhedra, such as tetrahedrons or octahedrons, whereas connection of vertices generates open structures that are edge-skeletons of such polyhedra. Platonic and Archimedean solids are part of a larger classification of polyhedra called uniform polyhedra. There is a subset of nine uniform polyhedra that have congruent edge-skeletons with the Platonic and Archimedean solids, but differ only in that they have both concave and convex faces, as shown in Figures 10A-10I. Of particular relevance to the subject invention are the convex faces of these nine polyhedra, which are a set of polygons connected at their vertices and have both open and closed faces. The resulting nine closed sets of polygons that are sustained by vertex-linked triangles, squares, pentagons, or combinations thereof, are termed “faceted uniform polyhedra.”

[0085] As shown in Figure 1, there are at least three faceted uniform polyhedra that can be generated by linking the vertices of only squares. From a design and control perspective, the most important consideration about faceted polyhedra is the dihedral angle between the planes of the polygons that are linked at their vertices. In the case of the three faceted uniform polyhedra that can be built from squares only, which one occurs will be strongly influenced by the angle subtended by the “spacer” moiety that links the vertices, *e.g.*: cubohemioctahedron (90°), small rhombihexahedron (120°), and small rhombidodecahedron (144°). Therefore, judicious control of the angle subtended by the vertices of the squares affords control over which polyhedron will

result. Representative ligands for each angle include, but are not limited to, those ligands shown in Figures 2A-2NN for 120° and Figures. 3A-3G for 144°.

[0086] Figure 4 shows a molecularly square-shaped nanoscale secondary building unit (nSBU). Square nSBUs can be described by the general formula: $M_2(RCO_2)_4$, where M is selected from a group that includes any transition metal, Group I metal, Group II metal, Group III metal, Group IV metal, lanthanide or actinide metals; and R is selected from any moiety that contains an additional carboxylate unit.

[0087] The molecule shown in Figure 4 has heretofore been known and is present in the Cambridge Structural Database. However, in the instant invention, the use of benzene-1,3-dicarboxylate (bdc) and 1,3,5-benzene tricarboxylate (btc) complexed with Cu(II) produced novel infinite and discrete architectures.

[0088] The molecular polygons that can be used to construct the molecular polyhedra and polymeric structures of the subject invention include, for example, molecular squares, molecular triangles, molecular pentagons, molecular octagons, molecular hexagons, and molecular n-gons. For example, squares, triangles, and pentagons can be utilized to construct molecular polyhedra of the subject invention. Octagons, hexagons, and n-gons can be utilized to construct the 2-dimensional structures of the subject invention.

[0089] The molecular polyhedra of the subject invention can be used in a great variety of industrial applications. For example, the molecular polyhedra of the subject invention can contain active chromophores in either, or both, the molecular building block and the linking moiety. For example, a coordinating ligand can be selected for chemiluminescence as well as its structural features, and a metal can be selected for its magnetic properties. Further uses for the molecular polyhedra of the subject invention can readily be found in the area of catalysis. Moieties known to be catalytically active in solution can be incorporated into the molecular polyhedra structures. For example, square planar metal moieties can be readily incorporated into $\{[XL_2Zn_2(btc)_1]_8[L_2Zn_2(btc)_{1.33}]_3\}_n$ or $\{[Zn_2(btc)_{1.33}]\}_n$. Rhodium and cadmium are metals also known to be catalytically active.

[0090] References to molecular polygons of various shapes (*e.g.*, triangle, square) are made throughout the subject specification. It will be understood by those of ordinary skill in the art that these shapes describe the approximate geometric structure of molecules in space (*e.g.*, conformation), which is based on the arrangement of bonds on each molecule's constituent

atoms. Angles of coordinating ligands are likewise based upon conformation. Conformational analysis of molecules can be carried out by those of ordinary skill in the art, using routine techniques.

[0091] The polyhedra and polymeric structures of the instant invention (and compositions comprising them) are useful in numerous applications because of their novel and desirable structures, and properties. For example, their inherent porosity can be exploited in gas storage, separations, chemosensors, biosensors, remediation of environmental pollutants, drug delivery, and other applications. The polyhedra of the subject invention can contain catalytic sites for use in homogeneous and heterogeneous catalytic processes. The polyhedra of the subject invention can exhibit high thermal motion, which makes them useful for liquid crystalline, lubricants, and thermoelectric materials. The polyhedra of the subject invention can exhibit magnetic properties, which make them useful for information storage or sensing. The polyhedra of the subject invention can have the ability to bind to biomolecules, making them useful in the formation of biomaterials, or for therapeutic applications. Polyhedra of the subject invention having excited state photochemistry make them useful as fluorescent or luminescent probes. The solubility of the polyhedra of the subject invention makes them useful as additives to polymers. In addition, their redox properties make the polyhedra of the subject invention useful for applications which require electron storage and/or transfer.

[0092] The terms “building blocks”, “polygon moieties”, and “molecular polygons” and “polygons” are used herein interchangeably to refer to those polygon-shaped moieties which contribute to the polyhedron-shaped structure of the polyhedron molecules and polymeric structures of the subject invention. More specifically, these terms are used herein to refer to a molecule that has external chemical functionalities which are arranged such that the functionalities can be considered to lie at the vertices of a polygon.

[0093] The terms “metal polygon”, “metal-organic polygon”, “metal building block”, “metal-organic building block”, “small or secondary building units”, “SBU”, “nanoscale SBU”, and “nSBU” are used herein interchangeably to refer to those building blocks comprising a metal-organic moiety.

[0094] The term “non-metal-organic polygon” and “non-metal polygon” are used herein interchangeably to refer to those building blocks which lack a metal-organic moiety.

[0095] The terms “linking moiety”, “linker”, and “spacer” are used herein interchangeably to refer to those moieties which connect vertices of two or more building blocks of the molecular polyhedra of the subject invention, and are intended to be inclusive of the terms “coordinating ligand” and “bridging ligand”.

[0096] The term “coordinating ligand” is used herein to refer to those moieties which connect vertices of two or more metal-organic polygons, such as through covalent interactions.

[0097] The term “bridging ligand” is intended to refer to those moieties which connect vertices of two or more non-metal-organic polygons, or which connect the vertices of a metal-organic polygon and a non-metal-organic polygon, such as through non-covalent interactions.

[0098] The term “0D” is used herein in its crystal engineering sense to refer to a structure that has finite dimensions in all three dimensions (also known as a discrete structure).

[0099] The term “1D” is used herein in its crystal engineering sense to refer to a structure that can be infinite in one dimension and has finite dimensions in two dimensions, such as a string.

[00100] The term “2D” is used herein in its crystal engineering sense to refer to a structure that can be infinite in two dimensions, and finite in one dimension.

[00101] The term “3D” is used herein in its crystal engineering sense to refer to a structure that can be infinite in all three dimensions.

[00102] All patents, patent applications, and publications referred to or cited herein are incorporated by reference in their entirety to the extent they are not inconsistent with the explicit teachings of this specification.

[00103] Following are examples which illustrate procedures for practicing the invention. These examples should not be construed as limiting. All percentages are by weight and all solvent mixture proportions are by volume unless otherwise noted.

Example 1—Synthesis of a Discrete Square SBU with Pyridine as Apical Ligand

[00104] Procedure: 0.232 g Cu(NO₃)₂·2.5H₂O (1 mmol) was dissolved in 4 ml of methanol. An additional solution of 0.244 g (2 mmol) of benzoic acid was dissolved in 4 ml of methanol along with 0.24 ml of pyridine (3 mmol). Both solutions were mixed together very slowly and left to sit under ambient conditions to allow for slow evaporation. After a day or two greenish-blue crystals were formed from the solution.

[00105] Analysis: Crystallography: $a = 10.134$, $b = 10.53$, $c = 17.46$, $\beta = 98.45$, space group: $P2_1/n$, $\text{Volm} = 1842.94$.

[00106] IR Spectrum: intense peak at 1395 cm^{-1} .

[00107] Solubility: soluble in dichloromethane, pyridine, and toluene/pyridine mixture.

[00108] Here, a molecule based on self-assembly of molecular squares formed a small rhombihexahedron by layering of methanolic $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and H_2bdc onto a solution of pyridine that contains templates such as nitrobenzene or 1,2-dichlorobenzene.

Example 2—Synthesis of a Spherical Discrete Crystal

[00109] Procedure: 0.232 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1 mmol) was dissolved in 4 ml of methanol and 3 ml of nitrobenzene. A second solution of 0.166 g (1 mmol) of 1,3-bdc was dissolved in 4 ml of methanol and 0.24 ml of pyridine (3 mmol). After slow diffusion of the 1,3-bdc solution over the $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ solution, greenish-blue crystals were formed within hours.

[00110] Analysis: Crystallography: $a = 26.17$, $b = 27.7607$, $c = 28.4356$, $\alpha = 92.719$, $\beta = 96.395$, $\gamma = 92.681$, space group: $P-1$, $\text{Volm} = 20478.5$.

[00111] TGA: around 40% weight loss before decomposition at around 250°C

[00112] IR Spectrum: three intense peaks at 1380 cm^{-1} , 1345 cm^{-1} , and 1520 cm^{-1}

[00113] XPD: broad XPD pattern has been observed

[00114] Solubility: sparingly soluble in common organic solvents but slightly soluble in boiling nitrobenzene.

[00115] The single crystals of $[(\text{L})(\text{S})\text{Cu}_2(\text{bdc})_2]_{12}$, where $\text{L} = \text{pyridine}$ and $\text{S} = \text{methanol}$, which formed as shown in Figures 5A-5G revealed a structure composed of vertex-linked molecular squares that had self-assembled into small rhombihexahedra. The schematic shown in Figures 5A-5D illustrates how the linking of molecular squares generates the edge-skeleton structure. This molecule contained pyridine ligands at the interior surface that were bonded to the metal ions located at the exterior surface and MeOH ligands at the interior surface metal binding sites. A schematic of this structure is shown in Figure 16.

[00116] It was also observed that the large bowl-shaped square and triangular voids or windows provided access to the interior of the molecule. Disordered solvent was found in these voids or windows and in the 1-nm^3 internal cavity, which was determined to be large enough to

encapsulate C₆₀. There was high thermal motion and disorder in the ligands and the guest molecules, but the structure of the core was determined to be well-defined and unambiguous. The molecular volume was determined to be greater than 10 nm³, and the molecular weight was 6.80 kDa.

[00117] Another embodiment is shown in Figures 6A-6J. In this instance, an isomer of the small rhombihexahedron described before is crystallized under similar conditions except that 2,6-dimethylpyridine, a non-coordinating base, is used instead of pyridine. The crystal structure formed is represented by [(S)₂Cu₂(bdc)₂]₁₂, where S = methanol. Here, the composition differs in the nature of the apically coordinated ligands on the SBU and the connectivity of the SBU. For ease of comparison, Figures 22A-22D show various orientations of an Archimedean faceted nanoball configuration, and Figures 23A-23G show various orientations of the isomer configuration of the Archimedean faceted nanoball.

[00118] An example of the conformation of a bdc ligand that produces the 0D nanoballs of the subject invention is shown in Figure 22.

Example 3—Synthesis of a Second Discrete Crystal

[00119] Procedure: 0.2326 g Cu(NO₃)₂·2.5H₂O (1 mmol) was dissolved in 5 ml of methanol and 3 ml of nitrobenzene. A second solution of 0.166 g (1 mmol) of 1,3-bdc dissolved in 5 ml of methanol, and 0.24 ml of 2,6-dimethylpyridine (3 mmol) was also prepared. After slow diffusion of the 1,3-bdc solution over the Cu(NO₃)₂·2.5H₂O solution, greenish-blue crystals formed after a day.

Example 4—Synthesis of a Third Discrete Crystal

[00120] Procedure: 0.2326 g Cu(NO₃)₂·2.5H₂O (1 mmol) was dissolved in 5 ml of methanol and 3-4 ml of 1,2-dichlorobenzene. A second solution of 0.166 g (1 mmol) of 1,3-bdc dissolved in 5 ml of methanol, and 0.24 ml of 2,6-dimethylpyridine (3 mmol) was also made. Slow diffusion of the second solution over the first solution again yielded green crystals.

[00121] Analysis of Examples 3 and 4: Crystallography: a = 28.2539, b = 28.2539, c = 28.5533, γ = 120, space group: P6₃/m, Volm = 19739.84.

[00122] TGA: around 38% weight loss before decomposition at around 250° C.

[00123] IR Spectrum: three intense peaks at 1380 cm⁻¹, 1341 cm⁻¹, and 1518 cm⁻¹

[00124] XPD: broad XPD pattern observed

[00125] Solubility: sparingly soluble in common organic solvents, except for isopropanol, ethyl acetate, DMSO, and DMF; and slightly soluble in nitrobenzene.

[00126] In this instance, the molecular weight was 6.23 kDa, and the molecular volume was approximately 10 nm³.

[00127] The structure formed by Example 2 exhibited body-centered cubic packing, and the structure of Examples 3 and 4 was hexagonal close packing. Molecular modeling indicated insignificant difference in terms of torsional strain between the two structures.

[00128] Other features of the instant crystals were: (a) they are neutral and soluble in organic solvents; (b) they are chemically robust because of the stability of the square SBU; (c) they are likely to be chemically diverse because of the ability to be made from a wide variety of metals, including magnetically active and catalytically active metals; and (d) they both have internal and external sites that are suitable for much larger structures by acting as the node of infinite networks or as the core of mesoscale dendritic structures, since their interior cavities can be accessed via triangular or square voids or windows, and they are bowl-shaped, which means they can contain organic or other chemical species as their guests. The thermal stabilities are consistent with their structures and molecular components. In addition, the crystals appear stable indefinitely when in contact with their mother liquor. When heated, weight losses of 36.9 and 38.3%, respectively, were observed, and this was consistent with corresponding loss of guest molecules. The samples do not remain as single crystals when heated. Loss of coordinated molecules occurs at higher temperatures.

[00129] In the presence of different templates, it is also possible to obtain very different supramolecular isomers. These are represented by the formula Cu₂(pyridine)₂(O₂CR)₄ SBUs. An example of this, [Cu₂(pyridine)₂(bdc)₂]_n, is shown in Figures 7A-7C. In this embodiment, a “pseudo-square grid” structure is formed from four SBUs to make a bowl-shaped nanoscale SBU. This bowl shape is the same type of shape having the curvature as in the previous structures, but since only four SBUs are used, the entire sphere is not formed. In this structure, as in the previous ones, the bridging bdc moieties orient to form the observed polymeric structure.

Example 5—Additional Discrete Spheric Crystal

[00130] Procedure: 0.2326 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (copper nitrate hemipentahydrate) (1 mmol) was dissolved in 5 ml of methanol and 3 ml of nitrobenzene. The second solution contained 0.166 g (1 mmol) of 1,3-bdc dissolved in 5 ml of methanol and 0.3 ml of 2,6-dimethylpyridine (3 mmol). Slow diffusion of the second solution over the Cu-containing solution produced greenish-blue crystals.

[00131] Analysis: Crystallography: $a = 33.8617$, $b = 36.8416$, $c = 29.5142$, $\beta = 93.456$, space group: $\text{C}2/\text{c}$, $\text{Volm} = 36752.45$.

Example 6—Additional Discrete Spheric Crystal

[00132] Procedure: 0.2326 g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1 mmol) was dissolved in 5 ml of methanol and 4 ml of nitrobenzene. The second solution was prepared from 0.166 g (1 mmol) of 1,3-bdc dissolved in 5 ml of methanol and 0.3 ml of 2,6-dimethylpyridine (3 mmol). After slow diffusion of the second solution over the first solution, greenish-blue crystals were formed.

[00133] Analysis: Crystallography: $a = 28.2457$, $b = 28.2457$, $c = 28.6669$, $\gamma = 120^\circ$, space group: $\text{P}6_3/\text{m}$, $\text{Volm} = 19806.87$.

Example 7—Additional Discrete Spheric Crystal

[00134] Procedure: 0.093 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (4 mmol) was dissolved in 5 ml of methanol and 3 ml of nitrobenzene. The second solution was made from 0.066 g (4 mmol) of 1,3-bdc dissolved in 5 ml of methanol and 0.12 ml of 2,6-dimethylpyridine (1.2 mmol). Again, diffusion of the second solution over the first produced greenish-blue crystals.

[00135] Analysis: Crystallography: $a = b = c = 27.6895$, space group: $\text{Im} - 3\text{m}$, $\text{Volm} = 21203.03$.

[00136] In addition to crystals derived from square SBUs, structures having SBUs that generate triangular shapes are also within the scope of the instant invention, as shown in Figures 9A and 9B. Whereas the SBU that generates the square is represented by $\text{M}_2(\text{RCO}_2)_4$, SBUs of the general formula $\text{M}_2(\text{RCO}_2)_3$ generate structures having triangular shapes. Again, M and R can be selected from the groups already stated. Examples of some of these shapes are shown in Figures 10A-10I, but other possibilities, as is readily ascertainable by those of ordinary skill in the art, are also herein contemplated. Representations of these structures are shown in Figures

11A-11F and Figures 15A-15F, and the porosities and packing of these structures are also depicted. The basic schematic for Figures 11A-11F is $\{[XL_2Zn_2(btc)_1]_8[L_2Zn_2(btc)_{1.333}]_3\}_n$, where L = pyridine or water, and X = NO_3^- . The schematic representation for Figures 15A-15F is $\{[L_2Zn_2(btc)_{1.333}]_{12}\}_n$, where L = water or pyridine again.

[00137] Another group of compounds is also derived from complexes of the angular trifunctional ligand benzene-1,3,5-tricarboxylate.

[00138] Referring again to Figures 11A-11F, the crystal structure of the compound reveals that it is composed of molecular squares and triangles that were formed by self-assembly into small cubicuboctahedra because two of the btc carboxylate moieties impose a 120° angle at the linkage between the polygons. These have six square faces and eight triangular faces, and the small cubicuboctahedra are fused with one another at the square faces because of the presence of the third carboxylate of each btc ligand. Thus, each square face is fused or shared with the square face of an adjacent small cubicuboctahedron, whereas each triangular face is linked to squares in such a manner that another, smaller polyhedron is generated. This smaller polyhedron is one of the other faceted polyhedra that can be sustained by vertex-linked triangles, which defines an octahemioctahedron. The framework exhibited is low density because the faceted polyhedra are inherently open and, therefore, define a porous structure.

[00139] An aspect of these uniform polyhedra that makes them desirable as nanoscale building blocks is that there is inherently a great deal of control concerning the framework geometries that they must adapt if they close-pack. For example, for combinations of Platonic and Archimedean polyhedra, there exist only eleven possible space-filling infinite frameworks. In addition, there are even greater restrictions for faceted polyhedra since they must pack such that each polygon is connected only by its vertices and does not share its edges. Indeed, the possible packing for faceted polyhedra is restricted to only three related space-filling architectures as shown in Figures 12A-12C: rhombicuboctahedra/cuboctahedra/cubes (1:1:3), as Figure 12A; rhombicuboctahedra/cubes/tetrahedral (1:1:2), Figure 12B; cuboctahedra/octahedral (1:1), Figure 12C.

[00140] Since the small cubioctahedron has a congruent edge-skeleton with a rhombicuboctahedron, as depicted in Figure 13A, it must adapt one of only two possible frameworks. Furthermore, only one of these frameworks can sustain vertex-only connected triangles and squares. It therefore follows that self-assembly of small cubicuboctahedra, or

alternately, self-assembly of triangles and squares by vertex sharing, can result in only one framework. The structure therefore is pre-ordained and, furthermore, is clearly prototypal for other frameworks that can be formed from other molecular triangles and squares. The dimensions of the small cubicuboctahedron are the same as the unit cell dimensions as there is only one small cubicuboctahedron per unit cell. The separation between opposite square faces is therefore 2.05 nm and the dimensions of the windows are approximately 0.9 nm. The overall structure contains channels and cavities that are entirely predictable based on the dimensions of the constituents. It is also noted that the dihedral angle of 125°16' would exist in a perfect small cubicuboctahedron, as shown in Figures 14A and 14B.

Example 8—Synthesis of a Discrete Crystal (OH-nanoball)

[00141] An OH-nanoball synthesized from the 120 degree dicarboxylate ligand shown in Figure 2B is described below.

[00142] Synthesis: 5g of 5-hydroxyisophthalic acid (27.5 mmol) and 6.39 g of copper nitrate hemipentahydrate (27.5 mmol) was dissolved in methanol (100 ml). 6.40 ml of lutidine (54.9 mmol) was added and the solution was stirred for 15 min under ambient conditions. Addition of diethylether (120 mL) to the solution resulted in precipitation of crude material (10.573 g), crystallization of which from dimethyl sulfoxide afforded the title compound.

[00143] Crystal data: Intensity data collected at 200 K. Tetragonal, space group I4/mmm, $a = b = 31.111(4)$, $c = 35.999(6)$ Å, $V = 34844(8)$ Å³, $Z = 2$, $D_c = 0.708$ g cm⁻³, $\mu = 0.778$ mm⁻¹, $F(000) = 7366$, $2\theta_{\max} = 42.08^\circ$ ($-30 \geq h \geq 31$, $-31 \geq k \geq 31$, $-36 \geq l \geq 21$). Final residuals (for 296 parameters) were $R_1 = 0.1531$ for 5170 reflections with $I > 2\sigma(I)$, and $R_1 = 0.2128$, $wR_2 = 0.4702$, $GOF = 1.679$ for all 49928 data. Residual electron density was 1.051 and - 0.592 e Å⁻³.

[00144] XPD: Broad peaks

[00145] TGA: Complex weight losses at 36.09, 136.31, 257.14, 334.46, 599.61° C.

[00146] IR (neat, cm⁻¹): 3217.73 (s, OH), 1633.73 (s, carboxylate), 1380.33 (s, carboxylate)

[00147] Solubility: Readily soluble in methanol, ethanol, *iso*-propanol and sparingly soluble in DMF and DMSO.

Example 9—Synthesis of a Discrete Crystal (NO₂-nanoball)

[00148] An NO₂-nanoball synthesized from the 120 degree dicarboxylate ligand shown in Figure 2C is described below.

[00149] Synthesis: Slow diffusion of 1 ml methanolic solution of 5-nitroisophthalic acid (0.2 M) and Cu(NO₃)₂·2.5 H₂O (0.2 M) into 1 ml methanolic solution lutidine (0.4M) yielded blue square crystals.

[00150] Crystal data: crystals do not diffract (indicative of nanoball structure).

[00151] XPD: Broad peaks (indicative of nanoball structure).

Example 10—Synthesis of a Discrete Crystal (larger sphere)

[00152] A larger nanoball synthesized from the 144 degree dicarboxylate ligand shown in Figure 3C is described below.

[00153] Procedure. 244 mg Cu(NO₃)₂·2.5H₂O in 5mL methanol was added to 165 mg N-methylpyrrole-2,4-dicarboxylic acid and 1mL pyridine in 5mL methanol. The solution was sealed and left under ambient conditions. Prismatic blue crystals formed within several days.

[00154] Crystal data: crystals do not diffract (indicative of nanoball structure).

[00155] XPD: Broad peaks (indicative of nanoball structure).

Example 11—Growth of Nanoballs on a Surface

[00156] Because the nanoballs of the subject invention are highly soluble in common organic solvents such as methanol, ethanol, 1-propanol, DMF, and hot acetonitrile, the microcrystals are suitable for growth on substrates such as mica or glass. This was confirmed by atomic force microscopy (AFM), which is known in the art as a widely used tool for the study of crystal growth and behavior on surfaces. Examples of data obtained include: size control of nanocrystals on Langmuir-Blodgett films, protein crystal growth, molecular and nano-tribology, statistical analysis of 2D crystal sizes, dopant effects on crystal growth, and annealing effects on crystallization. These AFM studies revealed that the microcrystals are of quite uniform dimensions and that they are stable even after mild heating.

[00157] Nanoballs were synthesized from the acid shown in Figure 2B and deposited on mica and glass substrates. AFM images of the products obtained for the mica surface, without thermal annealing, show increasing density of microcrystals with increasing concentration. The

microcrystals had an average height of 140 nm with a variation of 30 nm; the surface roughness (root-mean-square; RMS) was 56 nm. The average size was 1.3 μm with a variation of 0.4 μm .

[00158] In the case of films prepared on glass, observation on samples that were not thermally treated gave poor image quality even in the non-contact mode due to the presence of residual solvent forming a strongly bound contamination film. This contamination layer was removed by heating to 37° C or 75° C over 24 hours. AFM images of microcrystals on glass after annealing at 37° C and 75° C are shown in Figure 25 and Figure 26, respectively.

[00159] As shown in the figures, the roughness (RMS) is 236 and 261 nm. Image analysis shows an average size of 1.4 μm for the sample annealed at 37° C and again 1.4 μm for that annealed at 75° C, with the variances being 0.4 μm . The average heights were 500 and 600 nm, respectively. For the 37° C sample, the height values were randomly distributed about the average, but in the case of the 75° C sample, there was an apparent statistical distribution of heights at 300, 600, and 900 nm.

Example 12—A Square Lattice Formed From Square SBUs

[00160] Procedure: 0.2326 g Cu(NO₃)₂·2.5H₂O (1 mmol) was dissolved in 4 ml of water. An additional solution was made by dissolving 0.166 g (1 mmol) of 1,3-bdc in 4 ml of ethanol and 0.24 ml of pyridine (3 mmol). Green crystals were obtained after slow diffusion of the 1,3-bdc solution over the Cu(NO₃)₂·2.5H₂O.

[00161] Analysis: Crystallography: a = 18.7912, b = 128.7912, c = 16.8886, space group: P4/ncc, Volm = 5963.5

[00162] TGA: around 25% weight loss before decomposition at around 280° C

[00163] IR spectrum: intense peak at 1381 cm⁻¹

[00164] XPD: sharp high peak at below 10° in 2 θ and some other distinct peaks at above 10° in 2 θ

[00165] Solubility: sparingly soluble in common organic solvents.

[00166] An additional embodiment based on the bowl-shaped nanoscale with triangular SBUs is shown in Figures 8A-8C. Again, the generic formula [Cu₂(pyridine)₂(bdc)₂]_n applies, but the structure corresponds to a semi-regular tiling pattern based on triangles and hexagons, since instead of four units as above, three are used in this case. Because of the nature of the bowl-shaped SBUs and the required connectivity, the hexagons are open and the 2D sheets pack

in an eclipsed manner. Large solvent channels (1.35 nm in diameter) therefore exist parallel to the 2D sheet.

Example 13—A Kagomé Lattice Formed from Triangular SBUs

[00167] Procedure: 0.2326 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1 mmol) was dissolved in 6-7 ml of methanol, and then 0.256 g of naphthalene (2 mmol) was also dissolved in the same solution. A second solution containing 0.166 g (1 mmol) of 1,3-bdc dissolved in 6-7 ml of methanol and further containing 0.3 ml of 4-picoline (3 mmol) was prepared. Slow diffusion of the second solution over the first produced green crystals.

Example 14—Additional Kagomé Lattice Formed from Triangular SBUs

[00168] Procedure: 0.2326 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1 mmol) was dissolved in 6-7 ml of ethanol. Then 2-3 ml of nitrobenzene was added to that solution. A second solution containing 0.166 g (1 mmol) of 1,3-bdc dissolved in 6-7 ml of ethanol with 0.24 ml of pyridine (3 mmol) was prepared. Again slow diffusion of the second solution over the first yielded green crystals.

[00169] Analysis of Examples 12 and 13: Crystallography: $a = 18.6001$, $b = 18.6001$, $c = 26.2181$, $\gamma = 120$, space group: R32, Volm: 7855.29; $a = 18.62$, $b = 18.62$, $c = 19.804$, $\gamma = 120$, space group: P3c1, Volm: 5956.672

[00170] TGA: around 27% weight loss before decomposition at around 250° C

[00171] IR spectrum: intense peak at 1382 cm^{-1}

[00172] XPD: broad XPD pattern has been observed

[00173] Solubility: sparingly soluble in common organic solvents

[00174] It was also found that substitution of 2,6-dimethylpyridine for the pyridine produced similar results. These are described in Examples 5-7 and the structures obtained were the same as observed for the other square-based spheres.

Example 15—Additional Kagomé Lattice Formed from Triangular SBUs

[00175] Procedure: Slow diffusion of ethanolic copper (II) nitrate into a solution of bdc and pyridine in ethanol in the presence of an appropriate template (nitrobenzene, 1,2-dichlorobenzene or naphthalene) affords prismatic blue-green crystals of $[(\text{L}_2\text{Cu}_2(\text{bdc})_2)_3]_n$.

[00176] An ethanolic solution (7 ml) containing 166 mg 1,3-C₆H₄(CO₂H)₂ (1.00 mmol) and 0.24 ml C₆H₅N (2.97 mmol) was carefully layered onto an ethanolic solution (7 ml) containing 232 mg Cu(NO₃)₂·2.5H₂O (1.0 mmol) and an appropriate template (*i.e.*, 3 ml C₆H₅NO₂, 3 ml dichlorobenzene (1,2-C₆H₄Cl₂), or 5 mg C₁₀H₈). The solutions were left to mix by slow diffusion, and small bluish-green hexagonal crystals formed within days.

[00177] It should be understood that use of a template is optional. For example, the procedure described above can be carried out without a template under similar conditions as those of Example 10, without the addition of naphthalene.

[00178] The crystal structure as shown in Figures 8A-8C can be described as the result of self-assembly of triangular nSBUs to yield a nanoscale Kagomé lattice. Cu₂ dimers are positioned at the lattice points and are bridged via the bdc ligands, thereby generating large hexagonal cavities within the layer. The bowl-shaped nSBU facilitates efficient packing when the bowls are eclipsed, which results in eclipsing of the hexagonal cavities (0.91 nm effective diameter) and hexagonal channels of the same dimension. The layers are undulating due to the curvature imparted by the bdc moiety, have a 1.24-nm amplitude and overlap with adjacent layers by approximately 20%. The apical positions of the Cu₂ dimers are occupied by coordinated pyridine ligands, and highly disordered solvent molecules occupy the hexagonal channels (ca. 28% by weight). Thermal analysis (TGA/DSC) suggested that the included solvent and the pyridine ligands could be removed at ca. 200° C, and that the desolvated lattice is thermally stable to temperatures in excess of 300° C. The most intense peaks observed in X-ray powder diffraction (XPD) patterns from the bulk sample are consistent with those calculated from single crystal data.

Example 16—Additional Square Lattices Formed From Square SBUs

[00179] By variation of the crystallization conditions a phase based on square nSBUs, having the formula [L₂Cu₂(bdc)₂]_n, was obtained. An example of the conformation of a bdc ligand that produces 2D networks (square and Kagomé) of the subject invention is shown in Figure 23.

[00180] The magnetic properties of the structure described in Example 15 are shown in Figures 20A and 20B. Figure 20A shows the temperature-dependent susceptibility (χ) at a constant field (H = 0.1 Tesla) and Figure 20B shows the field-dependent magnetization at low

temperature (T = 5 K). The data exhibit rich structure that can be associated with the combined intra-dimer and inter-dimer magnetic interactions. Cooperative magnetism in Cu₂ dimer-based complexes has been studied in the past and known to predominantly exhibit antiferromagnetic coupling (Jotham, R.W. *et al.* [1972] *Dalton Trans.* pp. 428-438; Kato, M. *et al.* [1964] *Chem. Rev.* 64:99-148).

[00181] The temperature-dependent χ in Figure 20A shows a maximum just below 300K and a minimum at around 60K followed by an upturn at lower temperature. The data presented has been corrected for the diamagnetic contribution. The χ -T variation is consistent with cooperative magnetic behavior observed in dimeric copper complexes. A standard Bleaney-Bowers (BB) model (Bleaney, B. *et al.* [1952] *Proc. R. Soc. London, A* 214:451-465) was used to generate a fit and this is also shown in Figure 20A. The two main fit parameters are the intra-dimer (J) and inter-dimer (J') interaction terms. From this fit, the values of J = -350 cm⁻¹ and J' = -18 cm⁻¹ were obtained. This model also takes into account the presence of uncompensated moments that follow a Curie law. This accounts for the upturn in susceptibility for temperatures below 50K.

[00182] A clue as to the nature of the geometrically frustrated antiferromagnetic state for this compound is revealed in the M-H data shown in Figure 20B. A well-defined hysteresis loop was observed indicative of ferromagnetic behavior. The presence of hysteresis even at 300K was also confirmed. It has thus been demonstrated herein that, in accord with the subject invention, it is possible to arrange nanoscale molecular objects (not atoms) with precise control and achieve periodic magnetic nanostructures (Sun, S.H. *et al.* [2000] *Science* 287:1989-1992).

[00183] Within the context of the triangular Kagomé lattice, we can now attempt to understand the origin of the ferromagnetic-like response leading to magnetic hysteresis. The triangular lattice framework will result in disruption of perfect antiferromagnetic ordering by introducing spin frustration that leads to canted arrangement of spins. Of course, here the term spins refers to the moments of the individual dimers. Spin canting can lead to the appearance of effective weak ferromagnetic long-range order. It has also been pointed out that in low dimensional systems such as semiconductor quantum dots, molecular magnets *etc.*, electron correlation effects in an antiferromagnetic lattice can lead to flat-band ferromagnetism (Tamura, H. *et al.* [2001] *Phys. Status Solidi B* 224:723-725).

[00184] The structure described in Example 13 exhibits a different topology, the 2D square lattice that is shown in Figures 7A-7C. In this case, from geometry considerations, spin frustration is ruled out and this is reflected in the magnetic measurements shown in Figures 21A and 21B. To keep the comparison direct and simple, the χ -T and M-H data has been plotted using identical conditions as that of Figures 20A and 20B. These magnetic data are very similar to recent experimental results reported by other groups on Cu₂ dimeric complexes (Zhang, X.X. *et al.* [2000] *J. Appl. Phys.* 87:6007-6009). Theoretical fit using the BB model to the χ -T data in this case yields fit parameters, $J = -380$ cm⁻¹ and $J' = -85$ cm⁻¹. Of course, the striking feature is the lack of hysteresis for this system with the M-H data exhibiting a straight line representative of a more traditional paramagnetic behavior.

[00185] These results dramatically underscore the potential afforded by supramolecular chemistry for the design of molecular nanostructure assemblies with desirable physical properties and emphasize how the composition of a material is not the only feature one must consider when designing a phase that exhibits molecular magnetism.

Example 17–Polymers Based on Small Cubicuboctahedra

[00186] Procedure: A 10-ml solution of Zn(NO₃)₂·2H₂O (220 mg; 0.741 mmol) and 1,3,5-benzenetricarboxylic acid (220 mg; 1.05 mmol) in methanol was layered onto a 10-ml solution of nitrobenzene containing 0.23 ml of pyridine (2.8 mmol). Large single crystals formed within hours under ambient conditions.

Example 18–Polymers Based on Small Rhombihexahedra

[00187] Procedure: A 10-ml solution of Zn(NO₃)₂·6H₂O (202 mg; 0.679 mmol) and 1,3,5-benzenetricarboxylic acid (126 mg; 0.6 mmol) in methanol was layered onto a 10-ml solution of benzene containing pyridine (0.1 ml; 1.24 mmol). Large single crystals formed within hours under ambient conditions.

[00188] The crystal structure of Example 15, as illustrated in Figures 15A-15F, reveals a compound that consists of small rhombihexahedra, which have congruent edge-skeletons with the rhombicuboctahedron (Figures 13A and 13B), that are fused at the square faces. There is only one possible space-filling arrangement that generates a close-packed framework for these polyhedra, a structure that must be based on squares alone, dihedral angles of 120° (Figure 14B),

and the rhombicuboctahedron edge-skeleton: rhombicuboctahedra/cubes/tetrahedral (1:1:2), shown in Figure 12B. The small rhombihexahedron of Example 15 is slightly larger than the polyhedron of Example 14. It has a diameter of 2.3 nm, and the triangular windows have dimensions of approximately 0.9 nm.

[00189] The thermal stabilities of both Examples 14 and 15 appear to be consistent with their structures and molecular components. Crystals of the compounds appear stable indefinitely when in contact with mother liquor. Weight losses of 7.2 and 8.2%, respectively, are consistent with loss of methanol, which occurs under ambient conditions, and the samples remain crystalline, as confirmed by single crystal diffraction patterns. Greater weight losses and irreversible decomposition occurs upon heating and corresponds to further loss of methanol and pyridine molecules. The interconnectivity of the cavities in both structures is quite different, but the windows and free volume of the dissolved structures are similar.

[00190] In a further embodiment, spin-frustrated lattices were formed, these representing an attractive target that was found to exemplify the antiferromagnetic Kagomé lattice. This example of a nanoscale Kagomé lattice is a phase that is sustained by paramagnetic dicopper(II) spin pairs (metal dimers) positioned at the lattice point. One advantage of this particular phase is that it exploits the concept of self-assembly of nanoscale secondary building units, or nSBUs, and therefore offers a versatile system for which the effect of systematically substituting the molecular components can be evaluated.

[00191] As described above, the structures of the instant invention are useful in any application in which liquid crystals are used, for example, and particularly in which magnetic properties are desirable, such as for use in magnetic devices or other applications. In addition, the instant molecules can be used in conjunction with pharmaceuticals as adjuvants or carriers. Other uses include optoelectric materials, lubricants, catalysts, polymer additives, and any other material where liquid crystals are used.